

Vermicompost Buffering Capacity to Reduce Acidification of Pb and Cd Contaminated Inceptisols and Entisols

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ABSTRACT

Contamination of heavy metals on the soil leads to an increase in its acidity. Vermicompost application is commonly used to improve the properties of soil. The study was carried out to determine the reduction of the acidity in Pb and Cd contaminated soils under the application of vermicompost. Two laboratory experiments were set using Completely Randomized Design (CRD) with two factors. The first factor was soil samples, *vis* Inceptisols, and Entisols, and the second factor was the rates of vermicompost, consisted of 0, 5, 10, 15 g kg⁻¹. The treatment combination was repeated three times. The soils were pretreated with 10 mg kg⁻¹ Pb or Cd using Pb(NO₃)₂ and Cd(NO₃)₂. Three hundred kg soil sample was incorporated with vermicompost and placed in a 500 ml plastic bottle. The mixtures were incubated for eight weeks, and the moisture of the soil was maintained at field capacity. The acidity and soil temperature were monitored every week. The study indicated that Pb contaminated soil acidity increased to the sixth week of the incubation and decreased afterward. However, the acidity of Cd contaminated soil was consistently increased during the incubation. Treatment of vermicompost significantly lowered the acidity of both Pb and Cd contaminated soils. Contaminated Entisols had a higher response to the application of vermicompost than that of Inceptisols. This finding is significant in assessing acidity risk and possible management intervention for Pb and Cd contaminated soils.

Keywords: Acidity, cadmium, contaminated soil, lead, vermicompost

INTRODUCTION

Intensive and prolonged use of synthetic fertilizers and pesticides leads to the degradation of soils and environmental contamination. Synthetic fertilizer such as phosphate fertilizer contains many heavy metals, accumulating in the soil after some time. Mortvedt (1995) noted that, on average, rock phosphate had 25, 10, and 188 mg kg⁻¹ of cadmium (Cd), lead (Pb), and chromium (Cr), respectively. Other researchers also confirmed that Cd content in P fertilizer (SP36) was 11 mg kg⁻¹ of Cd (Setyorini *et al.* 2003). Gimeno-García *et al.* (1996) also suggested that the superphosphate contained 2.22 and 12.5 mg kg⁻¹ of Cd and copper (Cu), respectively. The fertilizer application eventually increases certain heavy metals in soil (Atafar *et al.* 2010; Al Kader 2015; Wei *et al.* 2020).

Heavy metal content varies among soil samples. Soil sample from Nairobi, Kenya has 59.92-

471.17 mg kg⁻¹ Pb, 0.31- 1.90 mg kg⁻¹ Cd and 21.37-81.17 mg kg⁻¹ Cr (Kinuthia *et al.* 2020). Another soil sample from Uttaradit Province, Thailand, contains 7.06-14.16 mg kg⁻¹ Pb, 9.74-20.12 mg kg⁻¹ Cu, and 20.25-27.11 mg kg⁻¹ Cd (Chattaong and Jutamas 2020). In Oromia Regional State Ethiopia, Ethiopia, Gebeyehu, and Bayissa (2020) found the soil had 37.93, 25.96, and 5.30 mg kg⁻¹ of Pb, Cu, Cd, respectively. Heavy metal content is dependent on the agroecosystem and season during the year (Osobamiro and Adewuyi 2015; Guo *et al.* 2013). Heavy metal solubility in the soil is highly dependent on pH and their concentration (Salam and Helmke 1998; El Sayed *et al.* 2010). Most of the heavy metal content is surpass the limit recommended by WHO (Chattaong and Jutamas 2020).

Heavy metal contamination also increases the acidity of the soil. A study on lead (Cruywagen and Van de Water 1993) confirmed that Pb's hydrolysis produced a significant amount of hydrogen, causing an increase in acidity of the system. Barysz *et al.* (2004) also stated that heavy metals such as Zn, Cd, and Ag hydrolyzed, releasing protons.

Hydrolysis of Cd is also dependent on ionic strength (Soleimani *et al.* 2008). An increase in acidity of the soil will affect the productivity of the soil.

Soil organic matter content has a buffering capacity to prevent the acidification of the soil. Vermicompost is a source of organic matter which, upon its decomposition, will generate a humic substance. The humic substance is rich in the functional group, forms organo-metal complexes with heavy metal. The formation will lower the production of hydrogen. Several studies confirm that organic matter significantly reduces soil acidity (Mukhtar *et al.* 2018; Anggita *et al.* 2018; Sianturi *et al.* 2019; Mukhtar *et al.* 2016). The study aims to determine the acidity reduction of Pb and Cd contaminated soil under the vermicompost application.

MATERIALS AND METHODS

Experimental Design and Treatments

The study was carried out from July to October 2020 in the Soil Science Laboratory, Faculty of Agriculture, the University of Bengkulu. Two experiments were set using pretreatment of lead (Pb) and cadmium (Cd). A Completely Randomized Design (CRD) with two factors and three replications are employed in the two experiments. The first factor was soil samples, consisting of Inceptisols and Entisols. The second factor was vermicompost rates, i.e., 0, 5, 10, and 15 g kg⁻¹. Each set of the experiment was assigned separately.

Soil Sample Collection

A soil sample was compositely collected from Beringin Raya Village, City of Bengkulu, at 5 m above sea level. The soil from the village was classified as Entisols (Psamment). Another soil sample was collected from Air Duku Village, Rejang Lebong District, Bengkulu Province, at 1054 m above sea level, approximately 105 km away from the city. The soil was classified as Inceptisols (Andept). Both soil samples were taken from 0-20 cm depth, air-dried for two days, ground, and sieved with a 2 mm screen. The Inceptisols contained 28.6 g kg⁻¹ Total Soil Organic Carbon (TSOC), 1.90 g kg⁻¹ Total Soil Nitrogen (TSN), 4.97 mg kg⁻¹ available P, 0.074 g kg⁻¹ exchangeable K, 0.22 g kg⁻¹ exchangeable Ca, 0.028 g kg⁻¹ exchangeable Mg, 10.33 cmol_c kg⁻¹ Cation Exchange Capacity (CEC), 11.10% clay, 34.94% silt, and 53.96% sand with soil pH of 5.12. Meanwhile, the Entisols had 23.4 g kg⁻¹ Total Soil Organic Carbon (TSOC), 3.20 g kg⁻¹ Total Soil Nitrogen (TSN), 5.27 mg kg⁻¹ available P, 0.094 g kg⁻¹ exchangeable K, 0.018 g kg⁻¹ exchangeable Ca,

0.004 g kg⁻¹ exchangeable Mg, 8.54 cmol_c kg⁻¹ Cation Exchange Capacity (CEC), 8.48% clay, 10.54% silt, and 80.98% sand with soil pH of 4.47.

Vermicompost Preparation

Vermicompost was prepared as described by Mukhtar *et al.* (2017). The amendment was sieved using a 0.5 mm screen before its nutrient analysis. Nutrient content of the vermicompost was 7.98% C, 3.06% N, 5.96% P₂O₅, 1.27% K₂O, 1.79% Ca, 0.97% Mg, and pH of 5.47.

The Experimental Procedure

Three hundred g of each soil was weighed and incorporated with vermicompost according to the treatment. The mixture was placed into a 500 ml plastic bottle and pretreated with 10 mg kg⁻¹ Pb or Cd. Pb and Cd sources were Pb(NO₃)₂ and Cd(NO₃)₂, respectively. The mixture was watered using distilled water to field capacity. The mixtures, then, were randomly placed on a 150 cm high wooden table in the laboratory. Each set of the experiment was randomly assigned and seated at a separate table. The mixture was incubated for eight weeks, and the moisture content was maintained at field capacity by watering every day.

The temperature and pH of the soil were monitored every week. Soil pH was measured using a pH meter at a ratio of soil and distilled water 1:1 and converting to the soil solution's hydrogen concentration. Soil temperature was measured using a soil thermometer at a depth of 5 cm. At the end of incubation, the soil sample was air-dried, ground, and sieved with a 0.5 mm screen. The sample was analyzed for total soil organic carbon (TSOC) using Walkley and Black Method.

Statistical Analysis

Data were subjected to the analysis of variance using SAS University Edition at a probability level of 0.05. Treatment means were separated using factorial repeated measurement and the vermicompost effect using polynomial orthogonal.

RESULTS AND DISCUSSION

The Acidity of Pb Contaminated Soil

Lead contamination in soil significantly elevates the acidity of the soil. The acidity of Pb contaminated soil fluctuated during the incubation (Figure 1). There was a tendency of increasing acidity for the first three weeks of the incubation, then decreasing to the fifth week. The acidity continuously raised at seven weeks before decreasing to the end of the

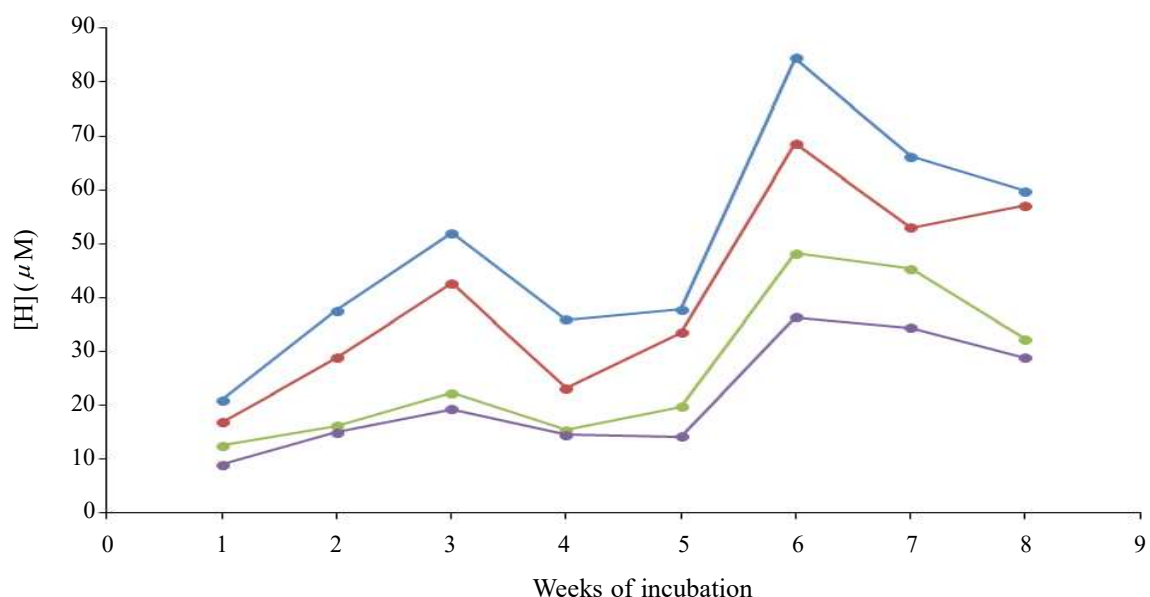


Figure 1. The effect of vermicompost on acidity during the incubation of Pb contaminated soil.
 —●— 0, —●— 5 g kg⁻¹, —●— 10 g kg⁻¹, —●— 15 g kg⁻¹.

incubation. The acidity of soil without vermicompost treatment increased by 63.45 mM in the sixth week compared to the first week, lowered by 24.64 mM after eight incubation weeks. Simultaneously, the acidity of soil treated with 15 g kg⁻¹ vermicompost increased only 27.36 mM at the first sixth week and reduced by 7.57 mM at the end of the incubation.

Vermicompost application significantly reduced the increase in acidity of Pb contaminated soil. The highest reduction of acidity was achieved by vermicompost application of 15 g kg⁻¹ (Figure 1). In the first week, the acidity of soil treated with the highest vermicompost rate was 132% lower than control (without vermicompost), while at the end of incubation, the reduction was 108%. Simultaneously, the acidity reduction at 10 g kg⁻¹ was 67% in the first week and 86% by the incubation end.

The vermicompost effect on Pb contaminated soil's acidity follows a linear pattern where an increase in vermicompost rate linearly decreases the acidity (Figure 2). The decrease in the soil acidity was more effective at Entisols than Inceptisols as indicated by the slope of the lines. Pb-contaminated Entisols' acidity lowered by 28.2 mM when soil treated with the highest rate of vermicompost while Inceptisol was only by 11.13 mM.

The Temperature of Pb Contaminated Soil

In general, during the incubation, Pb contaminated soil temperature was not significantly different among the vermicompost rates or the soil samples (Table 1). On average, the soil temperature was 299.2 °K, and the standard deviation of 1.00 °K, meaning that the soil sample's temperature was

Table 1. A soil temperature of Pb contaminated soil as affected by vermicompost.

Vermicompost (g kg ⁻¹)	Period of incubation (weeks)							
	1	2	3	4	5	6	7	8
	°K							
	Inceptisols							
0	299.7	300.7	298.7	297.7	299.3	299.3	299.0	299.0
5	298.7	299.7	298.3	297.7	299.7	300.3	299.7	298.7
10	298.3	299.7	298.7	298.0	300.0	299.7	299.7	299.0
15	299.0	300.0	298.7	297.3	300.0	300.0	300.0	299.3
	Entisols							
0	298.3	299.7	298.7	297.7	300.3	299.7	299.0	299.0
5	299.0	299.7	298.7	298.0	300.3	299.3	299.3	299.3
10	298.7	300.0	298.7	297.7	300.3	299.3	300.0	299.3
15	299.0	300.0	299.0	297.3	300.0	298.7	299.0	300.0

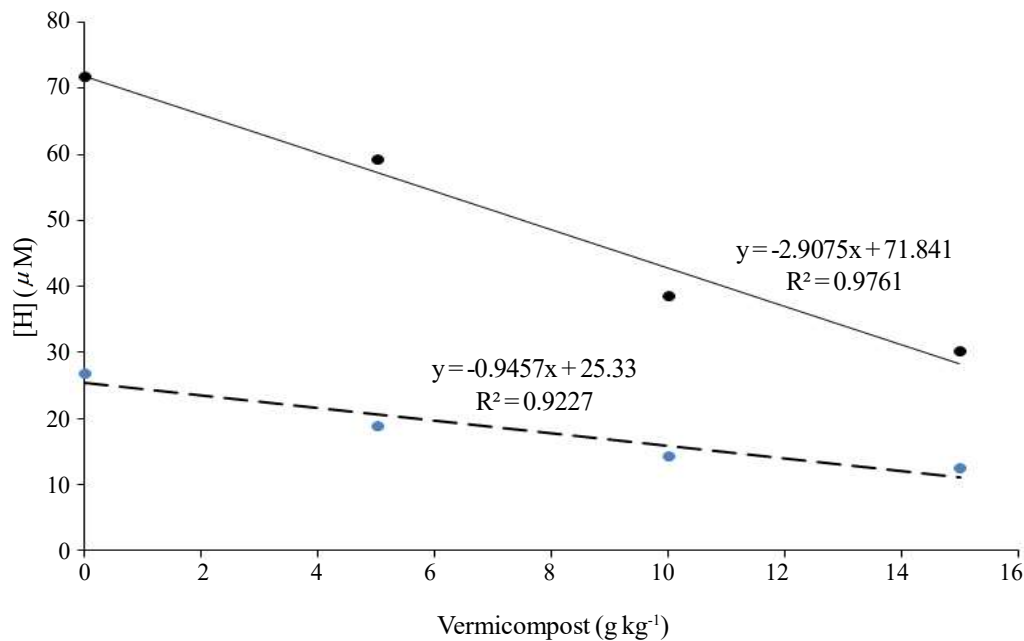


Figure 2. Vermicompost effect on the acidity of two Pb contaminated soil. — — Inceptisol, — Entisol.

very similar. A soil temperature of Pb polluted Inceptisols and Entisol ranged from 298.3 to 300 °K. This insignificant soil temperature indicated soil temperature had an identical effect on the reaction and decomposition of vermicompost.

The Acidity of Cd Contaminated Soil

Pretreatment of Cd to soil brought about the upraise of soil acidity, as shown in Figure 3. Unlike Pb contaminated soil, the acidity of Cd contaminated soil continuously increased during eight weeks of

incubation. A slight increase in the acidity was observed during the first four weeks and significant afterward. At the end of the incubation, Cd polluted soil without vermicompost treatment had the highest acidity (53.4 mM), which was 7.2 folds more elevated than that of the first week. Simultaneously, the acidity of soil treated with 15 g kg⁻¹ vermicompost was 19.58 mM, which was increased from 2.71 mM in the first week of incubation.

Vermicompost application continuously lowered the contaminated soil acidity from the first

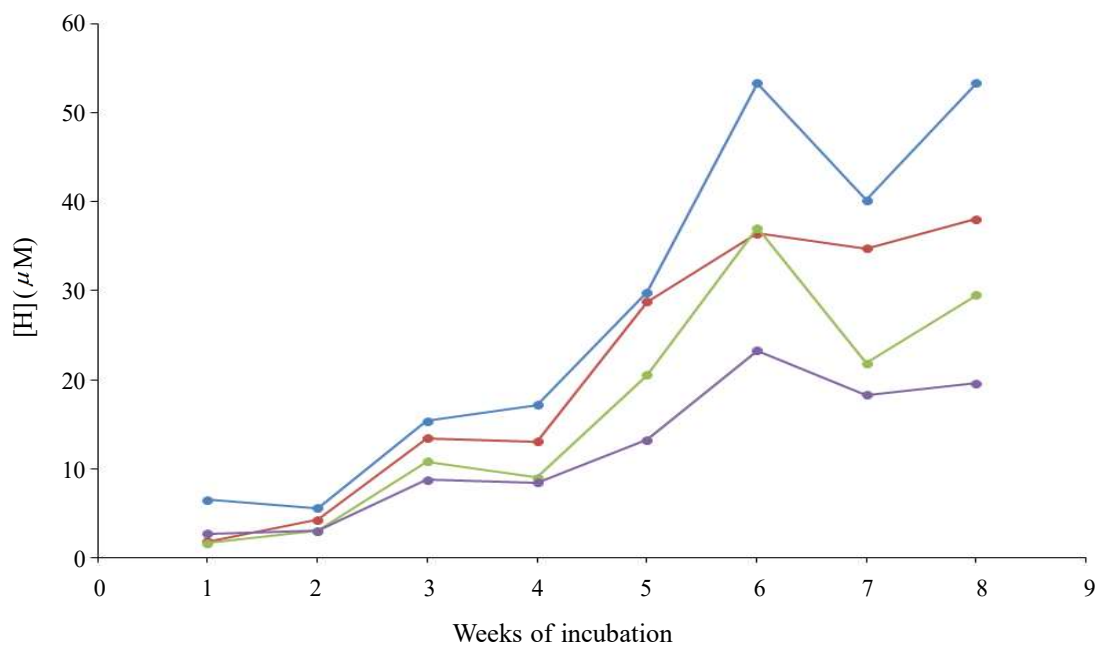


Figure 3. The effect of vermicompost on acidity during the incubation of Cd contaminated soil.

—●— 0, —●— 5 g kg⁻¹, —●— 10 g kg⁻¹, —●— 15 g kg⁻¹.

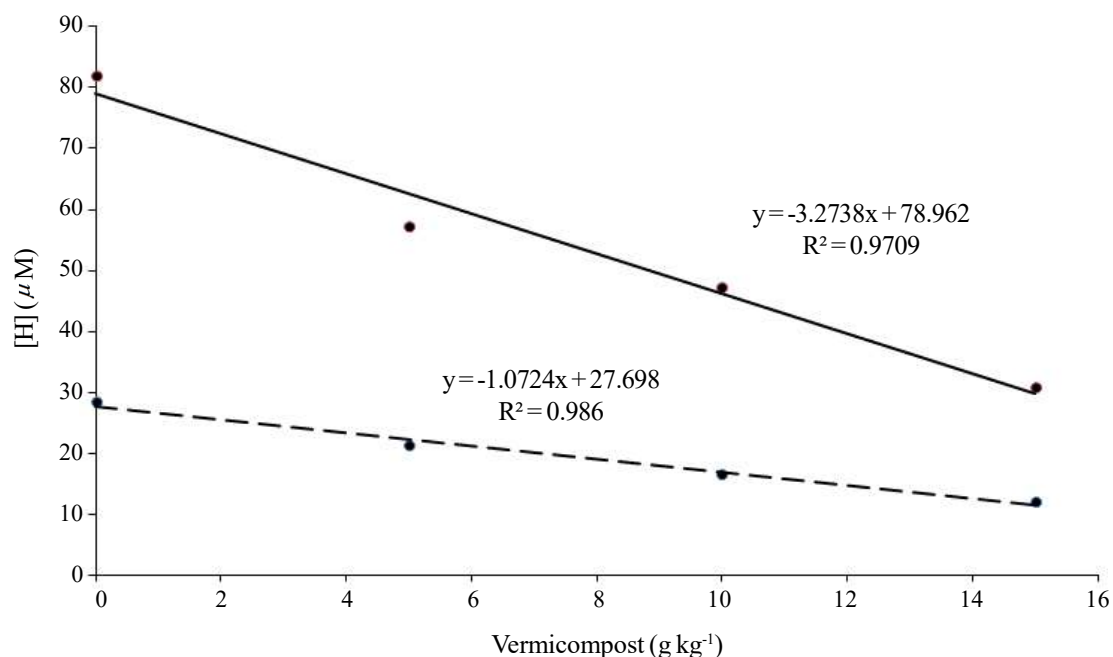


Figure 4. Vermicompost effect on the acidity of Cd contaminated soil. — — Inceptisol, — Entisol.

week to the incubation end (Figure 3). Higher differences in the acidity among control and vermicompost treated soils were observed as the incubation continued. In the first week, the acidity of soil treated with 15 g kg⁻¹ vermicompost 138% lower than control, while at the end of the incubation, it was 172% lower.

The application of vermicompost linearly reduced the acidity of Cd polluted soil, as indicated in Figure 4. As in Pb contaminated soil, vermicompost's effect was more effective for Entisols than Inceptisols, as confirmed by each linear line's slope. The line for Entisol's slope was -3.2738, meaning that an increase in 1 g kg⁻¹ vermicompost

lowered Cd contaminated Entisols' acidity as much as 3.273 mM. On the other hand, a similar rate increase in vermicompost for Inceptisols was only 1.0724 mM. The vermicompost application at the 15 g kg⁻¹ decreased by 166% for Entisols and by 134% for Inceptisols compared to control.

Like the temperature of Pb contaminated soil, the temperature of Cd polluted soil was not affected by vermicompost application (Table 2). In general, soil temperature ranged from 298.0 °K to 300.7 °K with a standard deviation of 0.82 °K. The soil temperature will have a similar effect on the decomposition of each rate vermicompost and soil reaction.

Table 2. A soil temperature of Cd contaminated soils as affected by vermicompost.

Vermicompost (g kg ⁻¹)	Period of Incubation (weeks)							
	1	2	3	4	5	6	7	8
	°K							
	Inceptisols							
0	299.3	300.3	299.7	299.0	300.7	300.7	300.0	299.0
5	299.7	300.0	299.7	298.0	300.3	300.3	299.7	299.3
10	300.0	300.7	299.0	298.7	300.0	300.7	299.3	300.0
15	299.0	300.0	299.0	298.7	299.3	299.3	300.0	299.7
	Entisols							
0	299.3	299.3	298.7	298.0	299.7	299.3	300.0	300.0
5	299.3	300.0	299.0	298.7	300.3	300.3	299.3	300.0
10	299.3	300.7	300.0	298.7	300.0	300.3	299.7	299.7
15	299.0	299.3	299.0	298.7	299.3	299.7	299.7	299.7

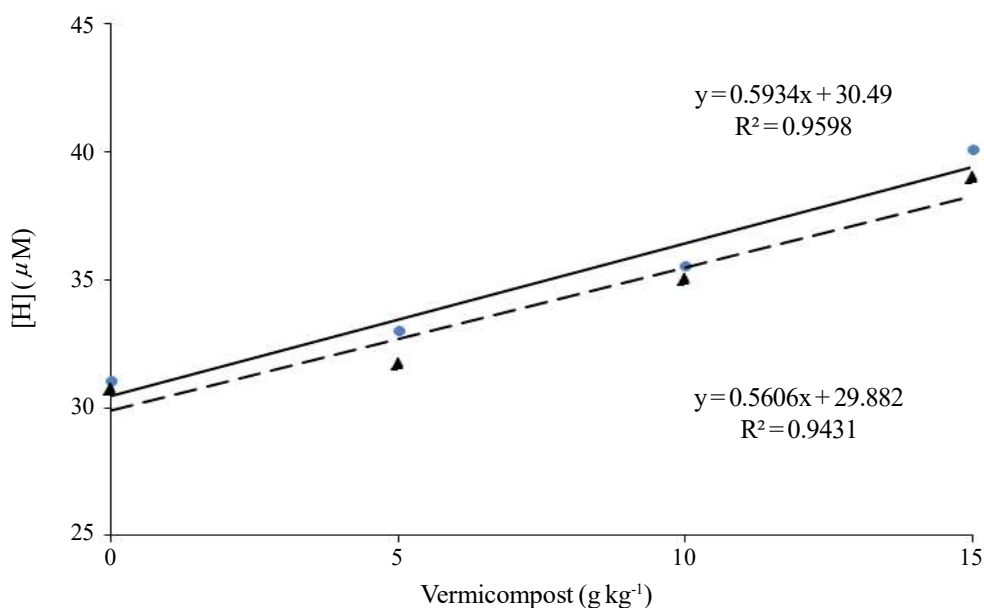


Figure 5. The effect of vermicompost on total soil organic carbon. — — Inceptisol, — Entisol.

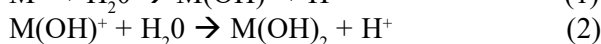
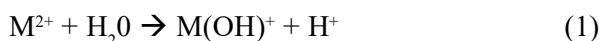
Total Soil Organic Carbon

Total soil organic carbon linearly increased as higher vermicompost treatment for both Inceptisols and Entisols (Figure 5). Application of vermicompost at the rate of 15 g kg⁻¹ raised TSOC by 29.1% and 28.1% for Inceptisols and Entisols compared to control. This result indicated that both soils had a similar response of TSOC on vermicompost treatment.

Discussion

Contamination of heavy metals such as Pb and Cd to soil has caused an increase in soil acidity. The results indicated that Pb contaminated soil's acidity continuously increased to the sixth week, then decreased to eight incubation weeks. However, a different pattern was observed for Cd polluted soil, where the acidity continuously increased to the end of the incubation. These results are associated with metals hydrolysis in soil solution.

Hydrolysis of Pb and Cd in the soil can be expressed in the following equations:



(Lindsay 1979; Cruywagen and Van de Water 1993; Barysz et al. 2004)

M Denotes Pb or Cd

Both reactions contribute hydrogen ions to the soil. The reaction will continue as hydrolysis proceed, and the production of hydrogen will also increase. The reduction of Pb contaminated soil acidity from

the third to fifth week may have been related to nitrate immobilization in soil. A previous study reported that nitrate was reduced to nitrite before being immobilized to form organic-N. During the reduced reaction of nitrate, the reaction requires hydrogen ion as following reaction $\frac{1}{2} NO_3 + H^+ + e^- \rightarrow \frac{1}{2} NO_2 + \frac{1}{2} H_2O$ ($Eh^0 = 0.834 V$ (Kizewski et al. 2019) leading to the reduction of acidity in the soil system. At the end of incubation, the reduction of acidity might lower the heavy metal hydrolysis.

Lead produces higher and faster hydrogen ions than Cd, as indicated in Figures 1 and 3. This result may have been attributed to their solubilities in soil solution where Pb is more soluble in water than Cd. The equilibrium constant of equation (1) for Pb is $2 \cdot 10^{-8}$, while that of Cd is $8 \cdot 10^{-11}$. The following reaction will be slower as the constant gets lower for each element (Lindsay 1979). Olajire et al. (2003) concluded that Pb is more soluble than Cd. As a result, the acidity of the contaminated soil significantly increases during the incubation.

Treatment of vermicompost significantly lowered the contaminated soil acidity (Figure 1, 2, 3, and 4). This result may have been related to the formation of the metal organo-complex. Vermicompost decomposition produces humic substances rich in carboxyl and phenolic functional groups, which are the soil's primary complexing agents (Sparks 2003). These functional groups have high-affinity heavy metals. A previous study confirmed that Pb and Cd were lower in the presence of humic acid (Wu et al. 2017; Baranèíková and Makovníková 2003; Peng et al.

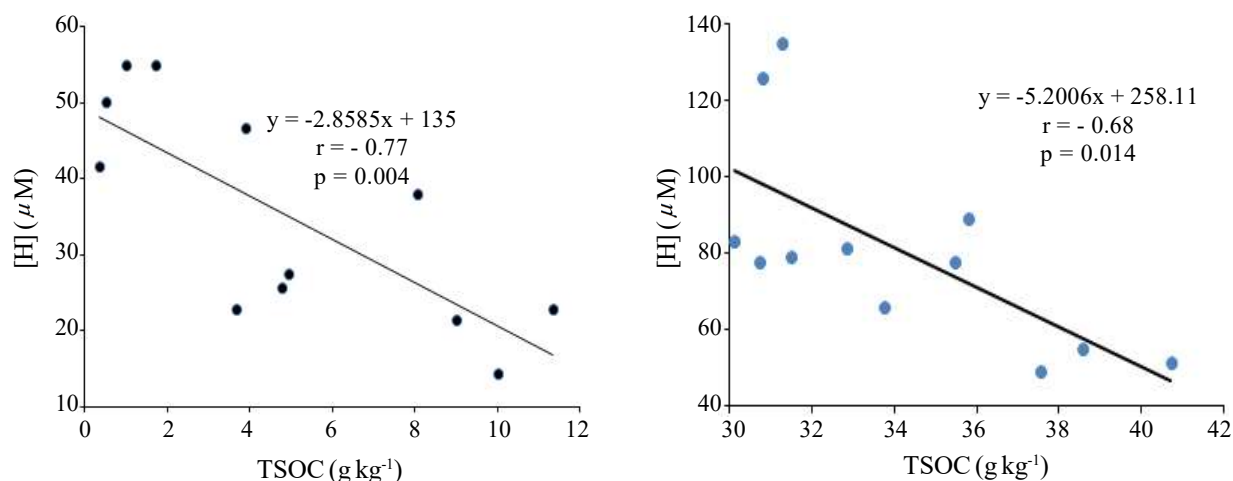


Figure 6. Relationship between TSOC and soil acidity of Inceptisols and Entisols.

2018). Other studies concluded that heavy metals such as Pb and Cd bound into the mineral-humic complexes (Qu *et al.* 2019; Klucakova and Pavlikova 2017). The binding of Pb and Cd consequently lowers their hydrolysis process and reduces hydrogen production to the system (lower acidity).

The vermicompost effect follows a negatively linear pattern where the highest reduction of the acidity was obtained at the rate of 15 g kg⁻¹ (Figures 2 and 4). This result is associated with vermicompost's organic carbon content, indicated by the increase in TSOC in soil (Figure 5). Several studies conclude similar results where the organic amendment decreases soil acidity (Uz and Tavali 2014; Z. Mukhtamar *et al.* 2018; Sianturi *et al.* 2019; Mahmud *et al.* 2018). However, other studies showed that organic fertilizer increased soil acidity (Wang *et al.* 2017; Manyuchi *et al.* 2013). The organic amendment effect on soil acidity is highly dependent on the initial content of the acidity. In this study, it is confirmed that soil acidity linearly decreases as TSOC increases with $r = -0.77$ ($p = 0.004$) for Inceptisols and $r = -0.68$ ($p = 0.014$) for Entisols as shown in Figure 6.

Each contaminated soil has a different response to vermicompost application, as shown in Figures 2 and 4. For Pb or Cd contamination, Entisols have a higher response to vermicompost application than Inceptisols as indicated by the linear line's slope. The result might have been due to the initial content of TSOC and clay content of both soils. Entisols have less initial TSOC (23.4 g kg⁻¹) than Inceptisols (28.6 g kg⁻¹) (Table 1). After application of vermicompost, Entisols consistently had lower TSOC than Inceptisols (Figure 5). Also, Entisols have lower clay content than Inceptisols, as indicated in

Table 1. The lower content of TSOC and clay of Entisols consequently have a higher response to vermicompost. Vermicompost will increase the buffering capacity to Entisol more than that of Inceptisols. A humic substance in vermicompost will act as a variable charge to buffer the soil's drastic change of acidity. A study by Jansen van Rensburg *et al.* (2009) concluded that organic carbon and clay are significant factors determining the soil's buffering capacity.

CONCLUSIONS

Contamination of Pb and Cd brought about an increase in the acidity of Inceptisols and Entisols. The acidity of Pb contaminated soils raised during the first six weeks and continuously decreased to the end of the incubation (eight weeks). However, the acidity of Cd contaminated soils increased steadily to eight weeks of incubation. Treatment of vermicompost increased the soils' buffering capacity and consistently reduced the acidity during the incubation. A higher rate of vermicompost had a more significant increase in the buffering capacity of the contaminated soils. Contaminated Entisols had a higher response to the application of vermicompost than Inceptisols. These findings could facilitate the assessments of acidification risks and potential management interventions, mainly heavy metal contaminated soils.

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